



## REGENERATION OF SPENT BLEACHING CLAY USED IN EDIBLE OIL REFINING IN SAUDI ARABIA

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### ABSTRACT

*Regeneration of spent bleaching clay used in edible oil refining in Saudi Arabia was studied using solvent extraction, boil-off method and calcination. The Solvent extraction method entails the removal of the oil using solvents. The effect of the solvent type, solvent to clay ratio (SCR), and extraction time on the percent of oil extracted (POE) and clay activity was investigated. The boil-off method entails the removal of oil by treatment with a boiling aqueous solution of sodium hydroxide under total reflux in the presence of NaCl. The effects of NaOH and NaCl concentrations, water to clay ratio (WCR) and time of reaction on POE and clay activity was investigated. Calcination entails the removal of the oil by heating at high temperatures. The effect of calcination temperature and time was investigated. The spent clay regenerated using either of these methods at optimum conditions was further activated by treatment with HCl or H<sub>2</sub>SO<sub>4</sub>. The effect of acid concentration and reaction time on clay activity was investigated.*

*It was found that calcination without acid treatment is sufficient to restore most of the clay activity. Boil-off method produces a clay with very low activity and further acid treatment enabled complete restoration of the activity of the clay. MEK was found to be the best solvent with respect to the activity of the deoiled clay. Further treatment of the clay deoiled using MEK with acids restored the activity of the clay.*

**Keywords:** *bleaching clay, regeneration, edible oils, calcination, acid treatment, solvent extraction.*

## **1. INTRODUCTION**

In edible oil and fat refining industries, degummed and neutralized oil is usually treated with bleaching clay to eliminate dissolved coloring material and to reduce the quantity of oxidizing matter. The spent bleaching clay represents a substantial amount of solid waste materials. The oil content can be as high as 35 wt.% of the spent clay. In the past dumping in landfills was used for disposal of spent bleaching clays. This is not allowed any more in most countries since it represents a source of odor problems and a fire hazard. The investigation of recovery of entrained oil and regeneration of spent clay is important for edible oil refining industry since it will enable clay recycling on one hand and on the other hand it will help abating environmental pollution.

There are several methods described in the literature to recover the oil retained in the filter residues. This recovery can be accomplished on the cake while it is still in the filter or after it has been removed from the filter [Ong, 1983]. It is a general practice to recover the fatty matter from the clay and discard the deactivated clay [Baily, 1982]. Solvent extraction processes for recovery of oil from bleaching residues have been suggested as they give a higher yield and better quality of oil than any other method, provided that the process is carried out on fresh residues. The deoiled clay may be reused in bleaching either directly or after activation with acids. Benzene is the preferred solvent for extraction; however, trichlorethylene is used when extraction with a non-inflammable solvent is inevitable [Hamza, 1966]. Solvent extraction followed by burning at 400°C is reported as one method that produces more active clay than the original [Hamza, 1966]. Others [Feuge and Ganssen, 1951] have described solvent regeneration of spent clay; organic solvents such as acids, ethers, ketones, etc., were used. A low molecular weight ketone was found to be the most effective solvent. Regeneration of deoiled spent clay by wet oxidation was investigated [Abulkalam and Joshi, 1988] using molecular oxygen as an oxidizing agent. Removal of sorbed oil from spent catalysts and other inorganic materials was reported [Fineyama, 1978]. Others [Smith, 1977] reported the cleaning of spent clay using aqueous alkali at high temperatures. The reactivation of spent bleaching clay using organic solvents were studied

[Kheoh, 1987]; preferred solvents are acetone and methylethylketone. A method to recover fatty acids from spent clay was described [Puri, 1981]. The treatment involves the saponification of the adsorbed oil by a solution containing an alkali and soap with pH greater than or equal to 10. A solvent extraction method to recover oil usable for food described [Sakakura, 1980]. Aqueous extraction was reported [Aoki and Nishigama, 1972]. A plant for the continuous recovery of oils and fats from decolorization sludge was described [Kokama, 1980]. He claimed that his method can produce oil and fats of high purity and can be used as food.

The amount of spent clay generated by edible oil refining industries in Saudi Arabia is estimated at 6000 tons per year [Alhamed and Al-Zahrani, 1999]. In this paper, a summary of our research [Al-Zahrani and Alhamed, 1995, 1996, 2000; Alhamed and Al-Zahrani, 1998, 1999] dealing with the regeneration of spent bleaching clay is presented.

A preliminary economical study of the regeneration of spent clay was published previously (Alhamed and Al-Zahrani, 1999). The study shows that the process is economically viable. Also, the quality of the extracted oil from the spent clay by the different solvents and its possible uses were discussed thoroughly by the authors (Al-Zahrani, A and Alhamed, 2000).

## 2. EXPERIMENTATION

### 2.1 Materials

Spent clay resulting from bleaching degummed American corn oil was obtained from Best Food Inc. at Yanbu and Saudi Vegetable Oil and Ghee Company (SAVOLA) in Jeddah. The bleaching clay consists mainly of alumino-silicate minerals. All the solvents used in this study were 99+% purity.

### 2.2 Spent Clay Regeneration by Solvent Extraction

#### 2.2.1 Solvent Screening Experiments

Solvent screening experiments were conducted in a Soxhelt extractor (Pyrex Buick Fit, Bibby Sterilin Ltd., England) fitted with a 500 ml flask and 150 mm high thimble chamber. 10.0 g of the spent clay was extracted with 200 ml of boiling solvent. After 30 siphons, the heating was stopped and the oil was separated from the solvent using a rotary vacuum evaporator. Residual solvent and moisture in the extracted oil was removed by drying in an oven at 105°C until a constant weight was obtained. Finally, the oil was cooled for 30 minutes in a desiccator and then weighed. The percentage of oil extracted (POE) was calculated as follows follows:

$$\text{POE} = (\text{Weight of Oil Extracted} / \text{Total Oil Content}) \times 100 \quad (1)$$

Soxhelt extraction experiments were conducted using the following solvents: petroleum ether (PE), methylethylketone (MEK), dichloromethane (DCM), benzene (B), ethanol (E), Chloroform (Chlf), trichloroethylene (TCE), methanol (Me), n-hexane (n-Hex), acetone (Ac) and benzene-ethanol mixture (B+E, 1:1 by volume).

The total oil content of the spent clay was determined by successive extractions of a 10 g sample of the spent clay with Methylethylketone (MEK) using Soxhelt apparatus. The total oil content was found to be  $23 \pm 2$  % of the spent clay weight. Further details are given in reference [Al-Zahrani and Alhamed, 2000].

### **2.2.2: Regeneration By Solvent Extraction**

The extraction unit consisted of a one-liter Pyrex glass vessel equipped with a variable speed glass-stirrer, heating mantel with temperature control, a condenser, a thermometer and sampling port. Briefly, the experimental procedure is described as follows: the required amount of the solvent (depending on the solvent to clay ratio) is placed in the reactor. 40 g of the spent bleaching clay is then introduced into the reactor and mixing started at the required speed. At the end of the experiment the reactor content is immediately transferred to the filtration apparatus to separate the clay from the solvent. The filtrate is transferred to a rotary evaporator for separation of the oil from the solvent. The separated oil is dried in a vacuum oven at 90 °C for one hour and allowed to cool in a desiccator then weighed to determine POE. More details about the experimental set-up and procedures are given elsewhere [Al-Zahrani and Alhamed, 1995, 2000]. The effect of extraction conditions (i.e. Solvent to Clay Ratio (SCR), time of extraction and mixing) on POE and percent bleaching (PB) was investigated.

### **2.3 Spent Clay Regeneration by Boil-off Method**

Regeneration using this method entails the oil removal from the spent clay by treatment with a boiling aqueous solution of sodium hydroxide (1-10% NaOH of the clay weight) under total reflux. NaCl (1-8% of the clay weight) is also added to the mixture in order to lower the surface tension between the oil and the clay. The effects of NaOH and NaCl concentrations, water to clay ratio (WCR) and time of reaction on POE were investigated. More details are published elsewhere [Al-Zahrani and Alhamed, 1996].

### **2.4 Spent Clay Regeneration by Calcination**

Direct Regeneration (without oil removal) of spent bleaching clay by calcination was studied in the temperatures range from 400 to 700°C and calcination time from 15 to 300 minutes. The required number of crucibles each containing 10 g of the spent clay are placed in a muffle furnace which has been heated previously to the desired temperature. A single crucible is then removed from the furnace at a predetermined time intervals. The samples are allowed to cool

down to room temperature in a desiccator to be used later for bleaching test or further activation by acid treatment.

## 2.5 Further Activation by Acid Treatment

Spent clays deoiled by solvent extraction, boil –off method or calcinations; at optimum conditions were further activated using H<sub>2</sub>SO<sub>4</sub> and HCl. A stirred batch reactor similar to that used in solvent extraction experiments was utilized for acid treatment studies. The effect of acid concentration (H<sub>2</sub>SO<sub>4</sub>: 2-25 wt.%; HCl: 2-15 wt.%), water to clay ratio (WCR= 1-5), time (0-2 hours) and temperature (25-105°C) of reaction, and mixing on the bleaching power of the reactivated clay was studied. Briefly, the experimental procedure was as follows: the required amount of the acid is placed in the reaction vessel and heated to boiling under total reflux to. 40 g of the deoiled clay is then admitted and stirring started at the required speed. Samples of 50 ml each were withdrawn at certain time intervals, and clay is separated by filtration, washed, then dried at 105 °C for one hour, cooled and finally used for bleaching refined corn oil. The color of the bleached oil is measured using Lovibond Tintometer model PFX990.

## 2.6 Determination of Percent Bleaching (PB)

Regenerated clays by any of the above methods were tested by bleaching of degummed corn oil that has a red color of 11.2. Bleaching tests were performed using an experimental setup similar to that reported by Kheok (1982). A Lovibond Tintometer (PFX990) was used for color measurements. The percent bleaching (PB) which compares the activity of reactivated clay to the fresh clay was calculated using the following expression:

$$\text{Percent Bleaching (PB)} = [(R_o - R_{fr}) / (R_o - R_{ff})] \times 100 \quad (2)$$

R<sub>o</sub> is the color of the refined degummed corn oil (unbleached) in red unit; R<sub>fr</sub> the color of the oil after bleaching with the regenerated clay in red units; R<sub>ff</sub> the color of the oil after bleaching with the fresh.

## 3. RESULTS AND DISCUSSION

### 3.1 Solvent Extraction Method

The results of the solvent screening experiments are summarized in Table 1. It is evident from this Table that POE, for the solvents used is in the order MEK > B + E > Ac > TCE = DCM. > Ch l>B > PE > n-Hex. The highest POE using soxhelt was obtained with MEK. The best four solvents in decreasing POE are: MEK, acetone, PE and hexane. Although, B+E, TCE, DCM, B and Chl gave POE values higher than n-Hex and PE, they were discarded due to their health and environmental hazards. The conditions under which the maximum amount of oil is extracted

using these solvents were determined as extraction time of 5 minutes, and SCR of 4 to 5 ml/g spent clay [Al-Zahrani and Alhamed, 2000].

Figure 1 compares the four solvents investigated with respect to their POE and PB at optimum deoiling conditions. As can be seen from this Figure, clay deoiled using MEK has the highest PB (77%) even without acid treatment. It is also evident that a strong positive correlation between POE and PB exists (i.e. PB increases as POE increases). This is easily explained by the fact that solvent treatment does not only remove the oil entrapped within the pore of the clay but also removes coloring matter strongly adsorbed on the surface of the clay and thus it can free these active sites. Depending on the solvent used (see Figure 1) PB values ranges from 77 down to 27. These values are still below the target of 100. Therefore it is clear that solvent extraction alone can restore most of bleaching ability of the clay. Further activation using acid treatment to improve the activity of the clay is warranted.

Table 1. Summary of solvent extraction experiments using Soxhelt [Al-Zahrani and Alhamed 2000)

Solvent	MEK	B + E	Ac	TCE	DCM	Chlf	B	PE	n-Hex	Me
POE	95.3	84.6	80.8	76.5	75.4	73	71.3	66.7	62.5	52.9

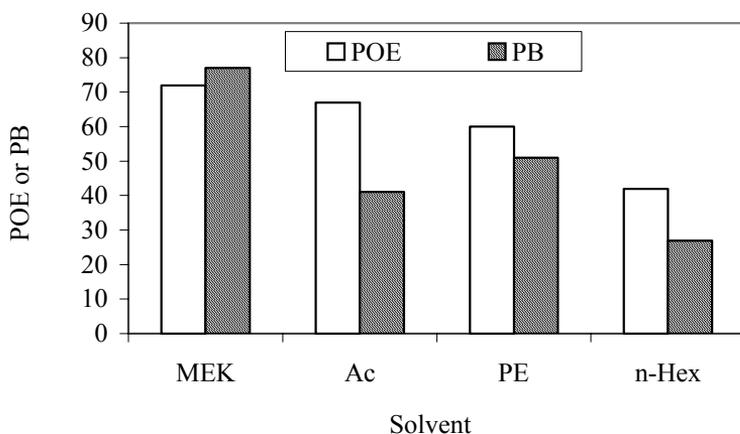


Figure 1: Comparison between POE and PB for various solvents.

### 3.2 Boil-off Method

Using the boil-off method a maximum oil recovery of 87% was obtained at following optimum conditions: 5 wt.% NaOH, 3 wt.% NaCl, WCR = 4 and a reaction time of 30 minutes. The effect of NaCl on oil recovery was negligible. The value of PB for spent clay

deoiled at these optimum conditions was 15.4% [Al-Zahrani and Alhamed, 1996]. This value is much lower than that obtained by regeneration using solvents. Although POE is higher than that obtained using solvent extraction (87 compared 72), PB value is very low. The reason for this may be due to the inability of this method of removal of strongly adsorbed coloring matter that block the adsorption sites on the clay surface.

### 3.3 Calcination

The effect of both temperature and time of calcination on PB of the regenerated clay is presented in Figure 2. It is evident from this Figure that for temperatures less than 600 °C, PB initially increases with calcination time then reaches a constant value for calcination times above 1.5 hour. For temperatures above 600°C, PB versus time curve passes through a maximum at about 1 hour then starts to fall gradually with increasing burning time. The optimum conditions which give maximum PB (91.4) are 550°C and 120 minutes. It is clear that by direct calcinations it was possible to restore most of the clay activity. The improvement in PB of the spent clay after calcination is attributed to the vaporization and combustion of organic compounds, coloring matter and oil adsorbed by and/or entrapped within the pores of the spent clay.

### 3.4 Acid Activation

Acid activation was performed for clays deoiled using solvents at optimum conditions and clay deoiled by boil-off method. Figures 3 through 5 show the effect of reaction time and acid concentration on PB for spent clay deoiled by acetone, MEK and Petroleum ether respectively. Regardless of the solvent used in the deoiling process the common feature between the three solvents is that long reaction times and high acid concentration have an adverse effect on the activity of the clay. This behavior is very clear from Figure 5 in which activation times as high as 300 minutes has been investigated. Generally, HCl is superior to sulfuric acid considering the shorter reaction time and the lower acid concentration required to achieve maximum PB. We can see also from these Figures that an optimum time and acid concentration is required to achieve maximum PB. The structure of the clay is destroyed due to its dissolution by the strong acid at high concentrations and long reaction time. Even for moderate concentration of acid long reaction time has a negative effect on the quality of the clay (i.e. lower PB). High acid concentration and long reaction time are not recommended from an economical point of view. Therefore, low acid concentration and short reaction time are desirable. By using H<sub>2</sub>SO<sub>4</sub>, and HCl a maximum percent bleaching of about 100% was obtained with clay deoiled using MEK. The optimum conditions for the former were 15 wt.% acid and 15 minutes reaction time and for the later they were 10 wt.% acid and 30 minutes reaction time.

For acetone and petroleum ether, the maximum PB value obtained was less than 85%. It is worth mentioning at this point that the oil recovered using MEK was larger in quantity and is characterized by a very dark color in contrary to that recovered when acetone or PE were used. This means that in the case of the two later solvents some more oil and more strongly

adsorbed coloring materials are still present in the porous structure of the clay. It seems that the oil and coloring materials left on the clay (when deoiling with acetone or PE) prevent the acid from reaching parts of the porous structure of the clay and thus lower PB is obtained.

The bleaching power of clay regenerated by boil-off method was very low (PB = 15.4) compared to fresh clay. Therefore, further activation with hydrochloric acid or sulfuric acid was conducted. Figure 6 shows effect of reaction time and acids concentration on PB for clay deoiled by boil-off method at optimum conditions. As can be seen from this Figure, the behavior is similar to that observed with clay regenerated by solvents. The highest PB value obtained was for sulfuric acid (PB = 104) which corresponds to acid concentration and time of reactions of 15% and 15 minutes respectively. For HCl, the maximum PB was around 100 and the corresponding concentration and reaction time were 10% and 30 minutes respectively.

## 5. CONCLUSIONS

The results of this work are summarized in Table 2. With reference to this Table, the following conclusions can be made

- Direct calcination without acid treatment is sufficient to restore the activity of the clay (PB = 91.4). Further acid treatment brings about very little improvement in the activity to justify this treatment. The only disadvantage of activation by calcination is the loss of oil and emissions associated with process of oil burning.
- Boil-off method produces clay with very low activity (PB = 15.4). Further acid treatment completely restore the activity of the clay.
- Reactivation of the spent clay with solvent extraction depends strongly on the solvent used. MEK was found to be the best solvent with respect to the activity of the deoiled clay (PB = 77). The highest PB obtained after acid treatment also depends on the solvent used. Again in this case also clay deoiled by MEK completely restored its original activity after acid treatment.

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Table 2: Summary of activity (PB) of spent clay regenerated using various methods

Method of activation	Maximum Percent Bleaching at optimum conditions		
	Without acid treatment	After acid treatment at optimum conditions	
		HCl	H <sub>2</sub> SO <sub>4</sub>
Calcination	91.4	97.1	98.6
Boil-off Method	15.4	103	104
Extraction with MEK	77	99	100
Extraction with acetone	41	87	86
Extraction with petroleum ether	51	90	85

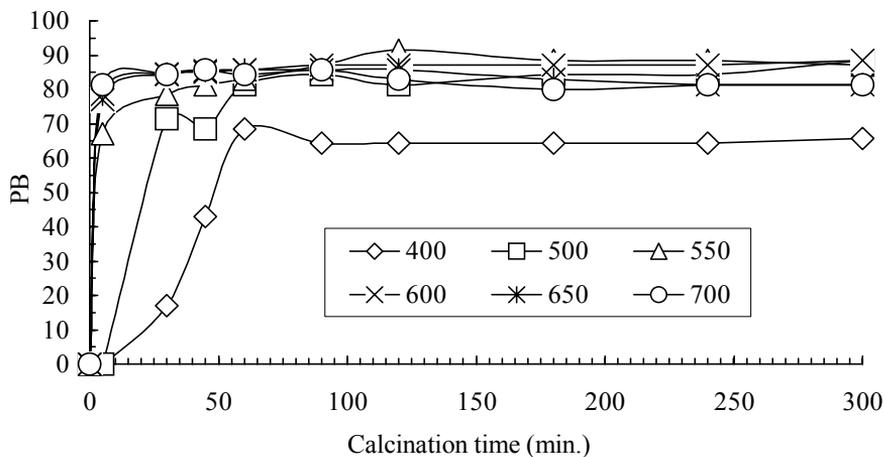


Figure 2: Effect of calcination time on percent bleaching (PB) at various temperatures.

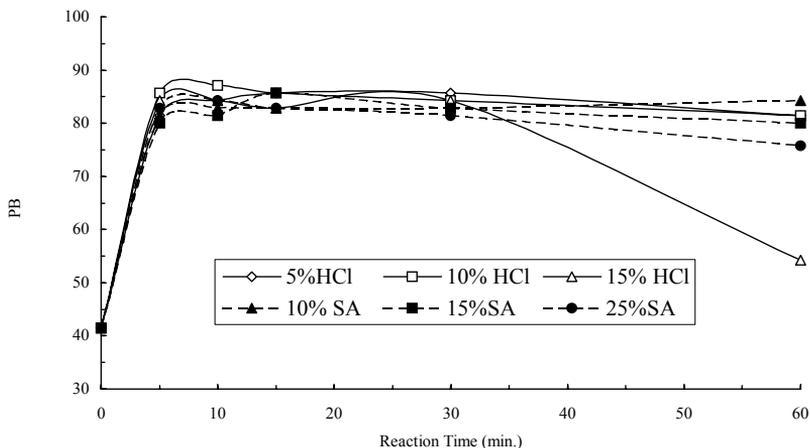


Figure 3: Effect of reaction time and acid (HCl or sulfuric acid (SA)) concentration on PB for clay deoiled by Acetone at optimum conditions. WCR = 5; RPM =200; Temperature = Boiling.

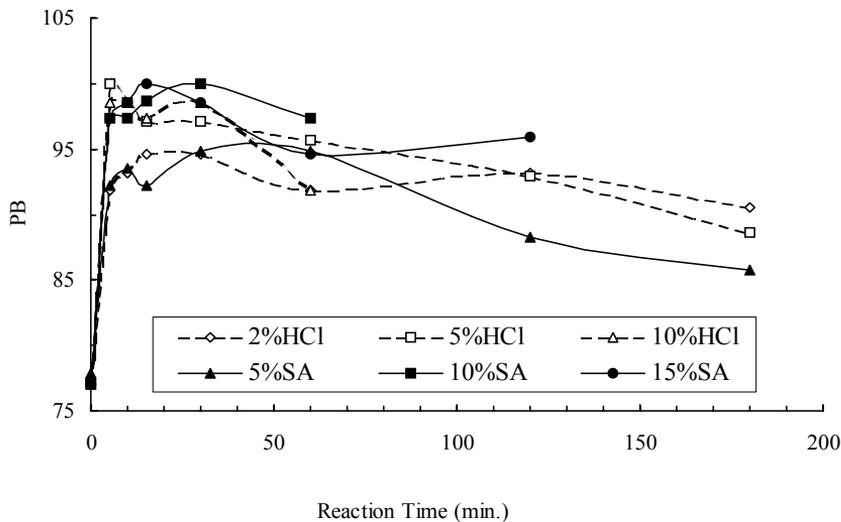


Figure 4: Effect of reaction time and acid (HCl and sulfuric acid (SA)) concentration on PB for clay deoiled by MEK at optimum conditions. WCR = 5; RPM =200; Temperature = Boiling.

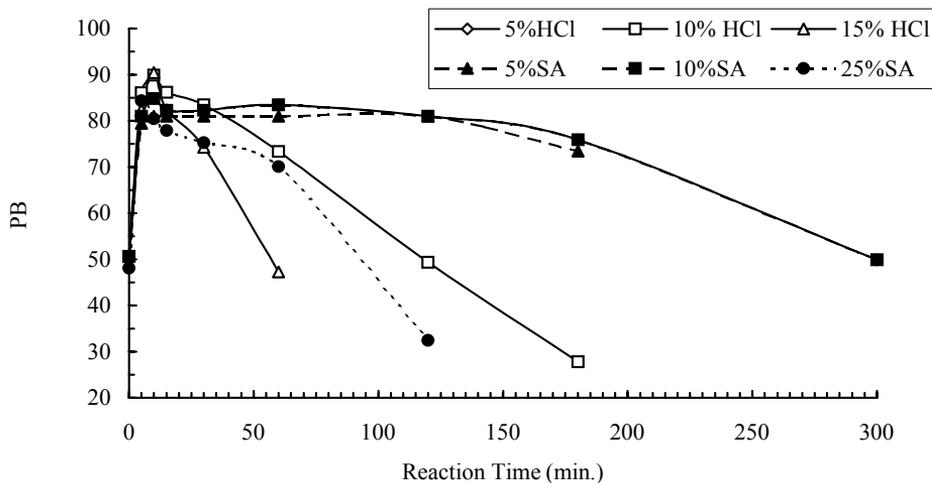


Figure 5: Effect of reaction time and acid (HCl or sulfuric acid (SA)) concentration on PB for clay deoiled by Petroleum ether at optimum conditions. WCR = 5; RPM =200; Temperature = Boiling.

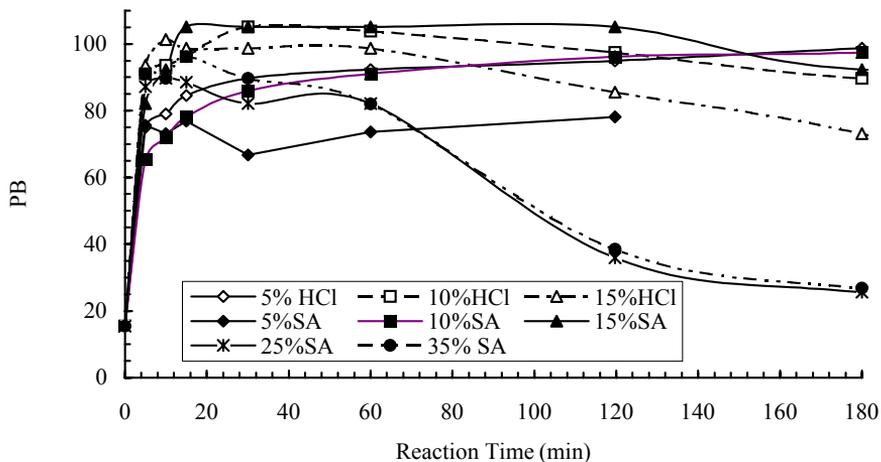


Figure 6: Effect of reaction time and acid (HCl or sulfuric acid (SA)) concentration on PB for clay deoiled by boil-off method at optimum conditions. WCR = 5; RPM =200; Temperature = Boiling.